

De Haas-van Alphen oscillations in the 12 Å-methylene blue intercalation compound of 2H-TaS₂

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 L385

(<http://iopscience.iop.org/0953-8984/11/32/102>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.220

The article was downloaded on 15/05/2010 at 16:57

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

De Haas–van Alphen oscillations in the 12 Å-methylene blue intercalation compound of 2H-TaS₂

A Schlicht, W Biberacher and A Lerf†

Walther-Meissner-Institut, Walther-Meissner-Str. 8, 85748 Garching, Germany

Received 10 May 1999

Abstract. We report on the first observation of de Haas–van Alphen oscillations in an organic intercalation compound of 2H-TaS₂. The 12 Å-methylene blue intercalation compound (12 Å-MB⁺-TaS₂) shows oscillations of the torque at magnetic fields higher than about 8 T. Four oscillation frequencies were observed at magnetic fields of 110 T, 257 T, 368 T and 876 T. The effective masses of the three orbits with the highest frequencies are 1.0, 1.2 and 1.4 electron masses, respectively. A simple rigid-band model fails in interpreting these results.

Although the intercalation compounds of the transition metal dichalcogenides belong to the class of quasi-two-dimensional metals, where quantum oscillations should be seen easily, the only compounds for which Shubnikov–de Haas oscillations have been reported up to now are the hydrated potassium intercalation compounds of 2H-TaS₂: K_x(H₂O)_yTaS₂ (Biberacher *et al* 1989). The potassium content x can vary from $x = 0.27$ to 0.4 if the host lattice is intercalated electrochemically. The content of the co-intercalated water y can be approximated as $y = 1 - x$. The intercalation process is a reduction reaction of the host lattice; for charge compensation of the cations between the layers electrons are transferred to the conduction band. The charge transfer n is given in units of TaS₂ and is in the case of the potassium (monovalent ion, fully ionized) intercalation compound equal to the cation content x (Butz and Lerf 1982).

For the binary host compounds 2H-TaS₂, 2H-TaSe₂ and 2H-NbSe₂ Shubnikov–de Haas and de Haas–van Alphen oscillations have been reported (Graebner and Robins 1976, Graebner 1977, Fleming and Coleman 1977, Hillenius and Coleman 1978). However, these compounds undergo a phase transition on cooling, and at low temperatures they are in a distorted lattice phase. This is usually assumed to be driven by a charge density wave (CDW). Recent theoretical calculations, however, assume this to be a metal–metal bond formation (Whangbo and Canadell 1992). For 2H-NbS₂, which shows no lattice distortion (Friend and Yoffe 1987), to the best of our knowledge no magnetic oscillations have been reported until now‡.

It has been reported recently (Hauptmann *et al* 1996) that three different intercalation compounds of methylene blue, named after their layer separation 9 Å-, 12 Å- and 17 Å-MB⁺-TaS₂, can be prepared electrochemically. In this article we report on torque experiments in all three compounds. In the 12 Å-methylene blue-TaS₂ (12 Å-MB⁺-TaS₂) compound we succeeded in observing de Haas–van Alphen oscillations. The charge transfer n of this compound can be estimated as $n = 0.12$. By comparing the oscillation frequencies of this material with the results of K_x(H₂O)_yTaS₂ the influence of the filling up of the conduction band on charge transfers from $n = 0.12$ to 0.4 can be studied.

† To whom correspondence should be addressed.

‡ One of us (WB) has failed to observe Shubnikov–de Haas oscillations of this compound in magnetic fields up to 20 T and at a temperature of 1.3 K.

The compound 2H-TaS_2 was prepared using a conventional vapour-phase transport reaction at 900°C via the 1T-form and a subsequent annealing procedure. The intercalation reaction was carried out using an electrochemical method under galvanostatic conditions out of deaerated aqueous solutions. For further details on the preparation of all three phases see Hauptmann *et al* (1996). The samples used for the measurements had an approximate mass of 1 mg. The charge transfer of $9\text{ \AA-MB}^+\text{-TaS}_2$ is $n = 0.06$ and the layer expansion Δd is 3.02 \AA (Hauptmann *et al* 1996). The 12 \AA -phase has a layer expansion $\Delta d = 5.9\text{ \AA}$ and the charge transfer can be estimated by comparing it with the 9 \AA -compound. As the layer expansion is doubled in the 12 \AA -phase the charge transfer should be doubled also, leading to $n = 0.12$. The estimate for the 17 \AA -phase leads to $n = 0.25$.

The magnetization measurements were carried out in a capacitive cantilever torquemeter described elsewhere (Christ *et al* 1994). The sample holder in use allowed an *in situ* rotation of the sample around one axis. The samples were fixed on the cantilever by a small amount of grease (apiezon N). Magnetic fields up to 14 T were provided by a superconducting magnet. The lowest accessible temperature was 0.5 K.

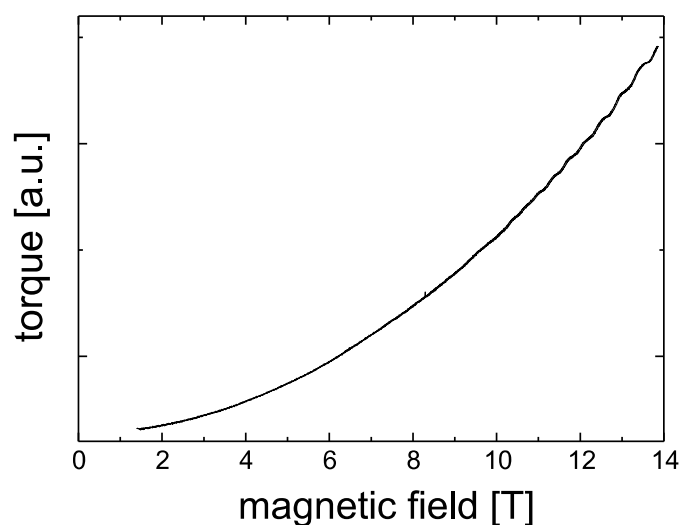


Figure 1. Torque, measured at an angle of 2.9° between the magnetic field and the c -axis of the crystal and at a temperature of 0.8 K.

Figure 1 shows the torque signal of the $12\text{ \AA-MB}^+\text{-TaS}_2$ compound at a temperature of 0.8 K. The angle θ between the magnetic field and the crystal c -axis was 2.9° . The main torque contribution shows a quadratic increase with the magnetic field. This is due to the anisotropy of the susceptibility parallel (χ_{\parallel}) and perpendicular (χ_{\perp}) to the layers (in the anisotropic case the torque is given by $\tau \propto B^2 \sin(2\theta)(\chi_{\parallel} - \chi_{\perp})$) (see, for example, Christ *et al* (1994)). A strong anisotropy of the susceptibility is reported for 2H-TaS_2 (Benchimol *et al* 1978). According to our measurements this anisotropy is not strongly affected by intercalation. For the 12 \AA -compound (figure 1) the quadratic contribution is temperature-independent. Superimposed on this quadratic background we observe an oscillatory signal, which is due to de Haas–van Alphen oscillations of the torque. At the lowest temperatures we can observe these oscillations starting from 8 T. The maximal signal height of the oscillation is about 2% of the steady torque. For the 9 \AA -compound we found a similar quadratic increase in

the static torque signal, but in this case a slight temperature dependence of the torque signal was observed, which is not understood at present and needs further investigation. It was not possible to resolve de Haas–van Alphen oscillations in this compound. The 17 Å-compound showed again a temperature-independent background signal. No oscillations could be observed.

As mentioned above, the angular dependence of the static torque signal should follow a $\sin(2\theta)$ law. This is very well fulfilled in our experiments for magnetic fields smaller than 6 T. For high fields and large angles a slight nonlinearity of the capacitance–torque relation occurs in our measurements. (The strongly linear regime is maintained for up to a 1% change in the capacitance (Christ *et al* 1994). In our experiments on the 12 Å-compound we observed a 6% change at 14 T and $\theta = 6.9^\circ$.) In contrast, the oscillatory torque is always so small that torque interaction plays no role (Shoenberg 1984). We did not observe second harmonics of any frequency. The de Haas–van Alphen frequencies themselves should in no case be influenced by the nonlinearity due to the background signal. For the determination of the cyclotron masses we chose small angles to avoid this problem.

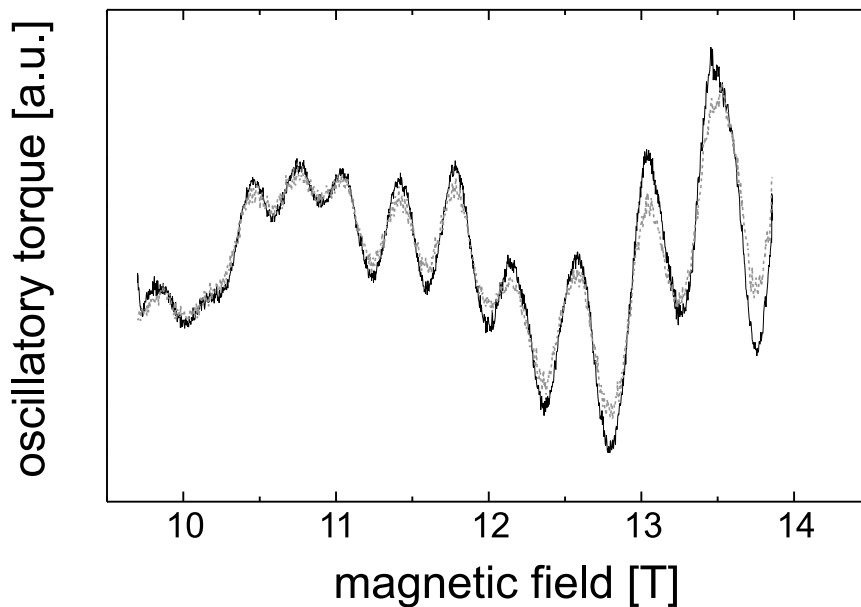


Figure 2. Oscillatory part of the measured torque at 6.5° for two different temperatures. The black line represents the measurement at 0.5 K and the grey the measurement at 1.4 K.

We now concentrate on the de Haas–van Alphen oscillations. Figure 2 shows the oscillatory part of the torque signal for $T = 0.5$ K and 1.4 K after subtraction of the quadratic background signal between 9.5 T and 14 T. The result of the Fourier analysis is shown in figure 3. Frequencies below 95 T are not shown because they were falsified by an improper subtraction of the static part. For an orientation of the field close to the direction perpendicular to the layers four oscillation frequencies of 110 T, 257 T, 368 T and 876 T were found. The cyclotron masses of the orbits belonging to these frequencies are 0.5, 1, 1.2, and 1.4 electron masses m_e , respectively. The error on these values is about $0.1 m_e$; only the 876 T oscillation has a larger error of $0.7 m_e$ because of the small amplitude.

It was possible to study the oscillations up to an angle of 28° (see figure 4). The line drawn in figure 4 is a fit to the data points of the 368 T oscillation represented by the function $F = F_\perp / \cos \Theta$. An estimate of the Dingle temperature from our data is not possible because

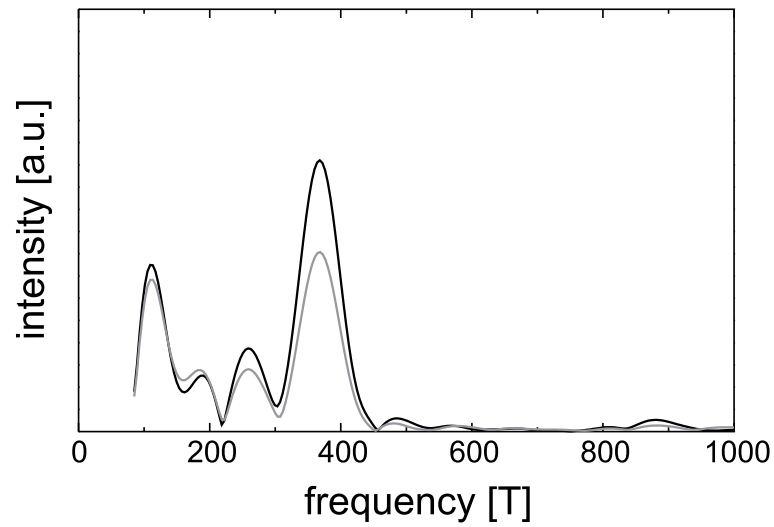


Figure 3. Fourier transforms of the oscillatory part of the torque between 9.5 T and 14 T for the data of figure 2. The black line represents the measurement at 0.5 K and the grey at 1.4 K. Frequencies lower than 95 T are not shown because they were falsified by an uncertain subtraction of the signal of the static susceptibility.

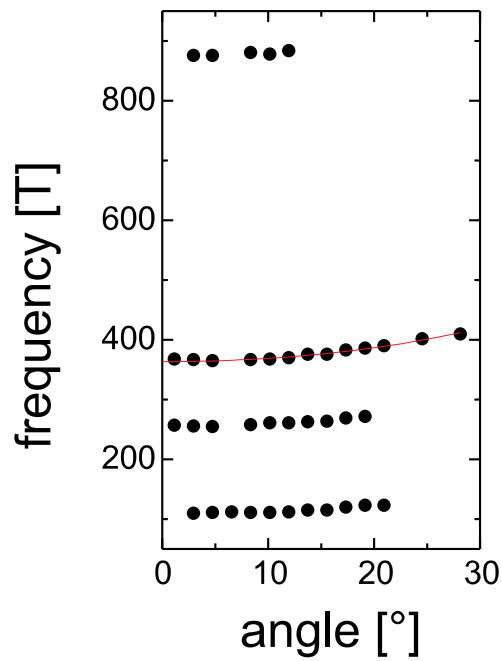


Figure 4. Angular dependence of the de Haas-van Alphen oscillations of $12 \text{ \AA-MB}^+-\text{TaS}_2$. The plotted line is a fit to the 368 T data representing the function $F_{\perp}/\cos \Theta$, the angular dependence expected for a cylindrical Fermi surface.

the magnetic field region, where oscillations could be seen, was too small to allow a meaningful analysis. The 368 T frequency is close to the sum of the 110 T and the 257 T orbits. Within our present study we cannot determine if this is a chance coincidence or due to magnetic breakdown; again, the field range where oscillations were observed was too small.

In order to observe oscillatory effects the mean free path of the electrons has to be long enough, namely one cyclotron orbit. Thus, the quality of the crystal indicated by a low Dingle temperature is important for the observation of oscillations. Biberacher *et al* (1989) estimate a Dingle temperature of $T_D = 3$ K for the potassium intercalation compounds, which is very high in comparison to other layered materials such as, for example, organic conductors (Wosnitza 1996) with $T_D \leq 1$ K. A reason for the high Dingle temperature is the mosaic spread of the host material, which is due to a structural phase transition of TaS₂ during the preparation of the 2H-phase via the 1T-form and still observable in the intercalation compounds. Thus it is not surprising that de Haas–van Alphen oscillations are not easy to detect in intercalation compounds of 2H-TaS₂.

When measuring the conductivity along the *c*-axis of intercalation compounds, it was found that this decreases with intercalation by about a factor of 10^3 (Thompson 1972). This means that the dispersion of the bands in this direction should decrease and the Fermi surface should become an almost perfect cylinder. In this quasi-two-dimensional case the angular dependence of the de Haas–van Alphen frequency is given by $F = F_{\perp}/\cos\theta$ (Shoenberg 1984). We could observe oscillations only up to $\pm 28^\circ$. Within this angular range we have a perfect agreement with the $1/\cos\theta$ -dependence. The angular range where quantum oscillations could be detected is larger than in the hydrated potassium intercalation compounds (Biberacher *et al* 1989), but it is still small compared to other quasi-two-dimensional compounds such as organic crystals (Wosnitza 1996). A possible explanation for this may be the mosaic spread of the crystals.

Because there are no band structure calculations available for any organic intercalation compound of 2H-TaS₂, we have to make model assumptions in order to discuss the observed frequencies. The simplest model assumed for intercalation compounds is a rigid-band model. The starting point is the calculated band structure of 2H-TaS₂ (see e.g. Guo and Liang (1987), Blaha (1991)). For the intercalation compounds these bands are kept rigid and the charge transfer is thought to fill up the conduction band. In the host 2H-TaS₂ the Fermi surface consists of undulating hole-like cylinders along the ΓA and KH directions in the hexagonal Brillouin zone (Wexler and Woolley 1976). The undistorted host should show oscillations in the frequency range between 4100 T and 6700 T. Because the Fermi surface is hole-like and electrons are added by intercalation the cylinders should shrink with increasing charge transfer. In a linear approximation a charge transfer of 0.12 electrons per TaS₂ unit should lead to a 12% reduction in the cross-sections of the cylinders. This means that the minimum frequency should be around 3600 T or higher. This is in contrast to the frequencies observed in this work, which are all less than 1000 T.

It is very likely that we do not see all parts of the Fermi surface, but the fact that several low frequency oscillations are present is not in agreement with a simple rigid-band model. Two conceivable effects can lead to oscillations with low frequencies: a commensurate superstructure of the intercalate layer, and a superstructure in the TaS₂ layers because of a structural instability like the one observed in the host material. A superstructure is not very likely to occur in the methylene blue intercalation compound, firstly because the dimensions of the dye molecule do not fit to the length of the *a*- and *b*-axis of the TaS₂ layers, and secondly there is no evidence for a structural instability in any intercalation compound, such as in 12 Å-MB⁺-TaS₂. Two facts support the last point: the transition temperature to superconductivity is 5.1 K, which is very high for organic intercalation compounds of

2H-TaS₂ (Subba Rao and Shafer 1979, Coleman *et al* 1983); and, the static susceptibility shows no temperature dependence (Schlicht 1999), as observed in 2H-TaS₂.

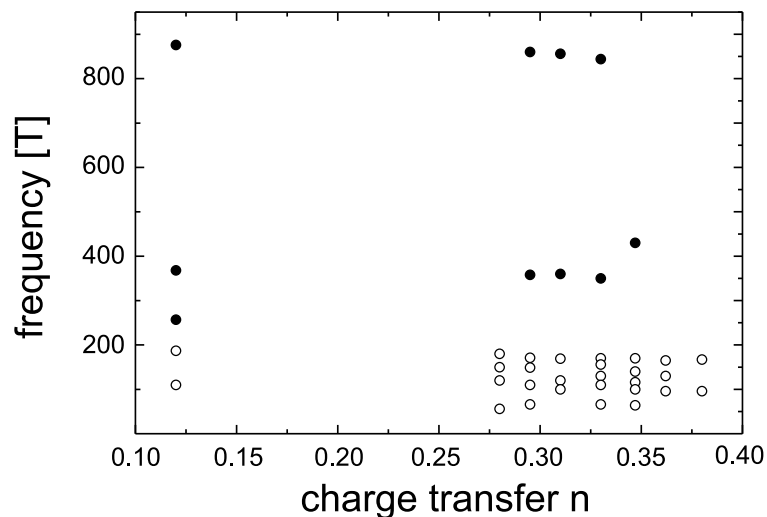


Figure 5. This figure shows the de Haas–van Alphen oscillation frequencies via charge transfer of the 12 Å-intercalation compound in comparison with the Shubnikov–de Haas oscillations observed in $K_x(H_2O)_yTaS_2$ by Biberacher *et al* (1989). The filled circles represent orbits with cyclotron masses more than $1 m_e$, the empty circles orbits with effective masses less than $0.55 m_e$.

Figure 5 shows the oscillation frequencies of the methylene blue intercalation compound ($n = 0.12$) in comparison with the charge transfer dependent results of Biberacher *et al* (1989) on $K_x(H_2O)_yTaS_2$ (other n -values). The observed oscillation frequencies are very similar. The high frequency oscillations decrease slowly with increasing charge transfer. The n -dependence of frequencies lower than 200 T cannot be established, especially as it was not possible to study frequencies lower than 100 T in this work. The MB^+ intercalation compound shows an additional frequency with an effective mass higher than $1 m_e$.

As pointed out by Biberacher *et al* (1989), there is strong experimental evidence that in the intercalation compounds an overlap of the valance band with the conduction band takes place. The different cyclotron masses of the orbits observed in the methylene blue compound as well as in $K_x(H_2O)_yTaS_2$ would be a further indication for this two-band model.

Finally, we have to discuss the fact that de Haas–van Alphen oscillations are only observed in the 12 Å-compound. The absence of oscillations in 17 Å- MB^+ -TaS₂ is probably due to bad sample quality. This phase is not very stable and could have partly transformed to the 9 Å-phase during sample mounting and cooling. This argument is not valid for the 9 Å-compound. From the results of our former experiments (Hauptmann *et al* 1996) we know that this is the most stable configuration. We can suggest two possible reasons for the absence of the quantum oscillations. Firstly, this compound is less anisotropic and shows a strong curvature of the undulating Fermi cylinders. According to the Lifshitz–Kosevich theory this would cause a smaller oscillation amplitude. Secondly, there is a temperature dependence of the background signal in this compound. This could be a hint that this phase is in a different ground state. To clarify these points experiments in higher magnetic fields are necessary.

We conclude that the normal state of the intercalation compounds is not yet understood. Many measurements can be interpreted with a two-band model, but as there are no band structure calculations it is not possible to relate the observed frequencies to calculated orbits. As the sum of the observed orbit areas is too low to represent the whole Fermi surface and there is no evidence for any superstructure occurring in these compounds, we assume that higher frequencies exist but could not be detected because of the poor Dingle temperature in these compounds and even higher effective masses of the missing orbits.

References

- Benchimol J L, Hedgcock F T and Di Salvo F J 1978 *Solid State Commun.* **25** 677
Biberacher W, Joss W, van Ruitenbeek J M and Lerf A 1989 *Phys. Rev. B* **40** 115
Blaha P 1991 *J. Phys.: Condens. Matter* **3** 9381
Butz A and Lerf A 1982 *Rev. Chim. Miner.* **19** 496
Christ P, Biberacher W, Müller H and Andres K 1994 *Solid State Commun.* **91** 451
Coleman R V, Eiserman G K, Hillenius S J, Mitchell A T and Vincent J L 1983 *Phys. Rev. B* **27** 125
Fleming R M and Coleman R V 1977 *Phys. Rev. B* **16** 302
Friend R H and Yoffe A D 1987 *Adv. Phys.* **36** 1
Graebner J E and Robins M 1976 *Phys. Rev. Lett.* **36** 422
Graebner J E 1977 *Solid State Commun.* **21** 353
Guo G Y and Liang W Y 1987 *J. Phys. C: Solid State Phys.* **20** 4315
Hauptmann A, Lerf A and Biberacher W 1996 *Z. Naturforsch. B* **51** 1571
Hillenius S J and Coleman R V 1978 *Phys. Rev. B* **18** 3790
Schlicht A 1999 *Normaleitende und supraleitende Eigenschaften von Farbstoff-Einlagerungsverbindungen des Wirtsgitters 2H-TaS₂* (München: Herbert Utz-Wissenschaft)
Shoenberg D 1984 *Magnetic Oscillations in Metals* (Cambridge: Cambridge University Press)
Subba Rao G V and Shafer M W 1979 *Intercalated Layered Materials* ed F Levy (Dordrecht: Reidel)
Thompson A H 1972 *Phys. Rev. B* **5** 2811
Wexler G and Woolley A M 1976 *J. Phys. C: Solid State Phys.* **9** 1185
Whangbo M H and Canadell E 1992 *J. Am. Chem. Soc.* **114** 9578
Wosnitza J 1996 *Fermi Surfaces of Low-Dimensional Organic Metals and Superconductors* (Berlin: Springer)